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(54) Title: PRODUCTION OF FLUOROPOLYMERS, FLUOROPOLYMER SUSPENSION AND POLYMER FORMED THEREFROM

(57) Abstract

Process for the production of fluoropolymers and/or copolymer resins thereof by the use of an aqueous dispersion system incorporating a redox initiator system which comprises t-butyl hydroperoxide and sodium metabisulfite to initiate the polymerization or copolymerization process. The process parameters may be controlled to provide a fluoropolymer or copolymer resin thereof having a desired target range of molecular weights. The process provides stable fluoropolymer dispersions which exhibit a low tendency to coagulate and further exhibit good wettability of the fluoro-homopolymer and copolymer particles, notably in the absence of soaps.

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# PRODUCTION OF FLUOROPOLYMERS, FLUOROPOLYMER SUSPENSION AND POLYMER FORMED THEREFROM

## Cross-Reference to Related Applications

This application is a continuation-in-part of application Serial Number 08/207,973, filed March 7, 1994, which in turn, is a continuation-in-part of application Serial No. 08/140,333 filed October 18, 1993, which in turn, is a continuation of application Serial Number 07/887,558 filed May 1, 1992, now abandoned.

## Background of the Invention

### Field of the Invention

The present invention relates to improved processes for the production of fluoropolymers and copolymers thereof; more particularly the present invention provides a novel redox system for the production of fluoropolymers and copolymers thereof which may be used in coatings and also in the formation of formed articles, i.e. films, resins, thermoformed articles, and the like wherein the fluoropolymers and copolymers thereof produced according to the present invention feature among other attributes, improved processability. The improved production process further provides an aqueous, soap-free shelf stable dispersion of fluoropolymers and copolymers thereof.

### Description of the Prior Art

The preparation of solid polymers of polychlorotrifluoroethylene (hereinafter sometimes

referred to as "PCTFE") is well known to the art as well as are PCTFE materials which further comprise copolymers including but not limited to CTFE-vinylidene fluoride, CTFE- tetrafluoroethylene, as well as CTFE-ethylene copolymers. These materials are described in detail, for example, in 3 Encyclopedia of Polymer Science and Engineering, (2nd. Ed. 1985) ["Encyclopedia"]. As therein described, articles and films formed from PCTFE materials exhibit desirable vapor barrier properties, good thermal stability and resistance to strong oxidizing agents.

There are presently known a plurality of processes which were suitable for the formation of the homopolymer, polychlorotrifluoroethylene, and its copolymers. High molecular weight homopolymers and copolymers of PCTFE may be prepared by free radical initiated polymerization either as bulk, suspension, or aqueous emulsion via the use of a suitable initiator system or in the alternative by ionizing radiation.

For the formation of PCTFE in an aqueous suspension process, a redox initiator system which comprises, for example, an alkaline metal persulfate as an oxidant, an alkaline metal bisulfite as a reductant, and metal salts such as ferrous sulfate, silver nitrate, or copper sulfate, which are known to be useful as accelerators to the redox reaction, may be used.

For the production of PCTFE by emulsion polymerization, emulsifiers, generally fluorocarbon and chlorofluorocarbon compatible emulsifiers, may be used.

For the formation of PCTFE by bulk polymerization, a peroxide may be used as an

initiator. Of particular note, useful peroxides which may find use are one or more of the group of: trichlor-acetal-peroxide, dichlorotrifluoro-propionyl peroxide, heptafluorobutyryl peroxide, as well as other acyl peroxides derived from fluorocarboxylic acids.

Also known to the art is the formation of copolymers of PCTFE, such as copolymerized PCTFE with vinylidene fluoride and/or tetrafluoroethylene which may be produced by either suspension or emulsion polymerization processes. Generally, however, the use of comonomers is such that the weight percentage of the comonomers is relatively low, i.e., generally comprising a minor proportion of the total polymer as it is known that the desirable vapor barrier properties are substantially degraded by the inclusion of excessive amounts of comonomers.

Other methods for the production of PCTFE homopolymers and copolymers (which are sometimes hereinafter generally referred to as "PCTFE polymers") include the processes for the production of PCTFE film forming and copolymer resins as described in U.S. Patent Nos. 2,705,706; 2,700,622; 2,689,241; 2,569,524; 2,783,219; 2,820,026; 3,640,985; 3,671,510; 3,642,754; 3,632,847; and 3,014,015.

While these processes provide useful methods for the production of PCTFE polymer resins, various shortcomings in one or more of these processes have compelled the development of further novel methods for the production of PCTFE polymer resins.

One such shortcoming in the prior art is the encapsulation of inorganic moieties from the initiating species which are known to produce a PCTFE polymer resin with a relatively high content of

residual ash, which limits the range of applications within which articles formed using the PCTFE polymer resin may be used. Such materials are known to have lower dielectric strengths which is often undesirable for use in electrical and electronic devices and/or packaging.

A further shortcoming in the prior art is that processes which may be used to form aqueous dispersions of PCTFE polymer resins typically require the use of a soap or a surfactant composition.

Therefore, it will become apparent to those skilled in the art that there remains a present and continuing need for the provision of stable water based fluoropolymer suspensions free of soap and for improved fluoropolymers such as PCTFE homopolymers and copolymers, which are: 1) suitable for the production of formed articles therefrom, or to be included in the structure of a formed article; or 2) can be prepared as a stable aqueous dispension in the absence of a surfactant or soap and thus be used as a fluoropolymer coating. There also remains a continuing need in the art for the production of improved fluoropolymers such as PCTFE homopolymers and PCTFE copolymers which feature improved machine processability, particularly in regard to conventional thermoforming and process equipment.

## Summary of the Invention

The present invention includes improved fluoropolymer polymer resins, highly stable aqueous dispersions, particularly PCTFE homopolymer and copolymer compositions, and processes for the production of improved fluoropolymers and copolymers

thereof, such as PCTFE homopolymer and copolymer compositions.

In accordance with this invention, there is provided a process for forming fluoropolymers or a copolymer of a fluoromonomer and at least one copolymerizable monomer which comprises the steps of:

(a) forming a polymerization reaction mixture comprising a fluoromonomer or a combination of a fluoromonomer and at least one copolymerizable monomer and a redox initiator system comprising a mixture of an alkyl hydroperoxide and an alkali metal metabisulfite in a reaction solvent comprising water; and

(b) polymerizing the monomer while maintaining the mixture at a controlled temperature to form a stable aqueous dispersion of the fluoropolymer or the copolymer.

Also in accordance with this invention, there is provided a stable, soap-free aqueous dispersion of a fluoropolymer or a copolymer of a fluoromonomer and a copolymerizable monomer produced by the above process, as well as such polymer or copolymer produced by such process. Moreover, this invention provides articles formed of such polymer and copolymers, including articles in which such polymer or copolymer are present in at least one layer.

In one aspect of the present invention there is provided a process for the production of fluoropolymer dispersions and homopolymer resins and/or PCTFE copolymer resins containing fluoromonomer by the use of an aqueous suspension system incorporating a novel redox initiator system which comprises t-butylhydroperoxide and sodium metabisulfite to initiate the polymerization or copolymerization

process. The parameters of the process may be controlled to provide a fluoropolymer resin having a desired target range of molecular weights.

In a further aspect of the instant invention there are provided soap-free, shelf stable fluoropolymer dispersions; these dispersions exhibit a low or no tendency to coagulate and further exhibit good wettability of the fluoropolymer and copolymer particles, notably in the absence of soaps.

In further aspects of the present invention there is provided a fluoropolymer dispersion and resin produced by the aqueous polymerization of comonomers utilizing a redox reaction of tert-butyl hydroperoxide and sodium metabisulfite; and control of the various constituents and the reaction condition provides for the controlled production of fluoropolymer resins having a desired molecular weight, desired molecular weight distribution, particle size and concentration.

In a still further aspect of the present invention there are provided fluoropolymer resin compositions which may be readily formed using conventional process equipment into formed shapes, film, sheets, as well as other thermally formed articles. In the alternative, the fluoropolymer resin composition formed by the process described herein may also be used to form one layer of a construction of an article, i.e., forming a barrier layer within a multilayer film structure or forming a barrier layer within a formed article.

Not only does this invention provide a resin having improved thermoformability and color, but it also provides a novel aqueous dispersion from which the resin is prepared, wherein the dispersion is free of surfactants, soap, and undesirable stabilizing

additives such as nonionic and ionic surfactants, defoamers, and known non-fluorinated polar functional monomers such as acrylic acid, which are known to impart stability to prior art aqueous dispersions.

**Description of the Preferred Embodiments**

The present invention provides for a novel process for the production of fluoropolymer resins and stable, soap free dispersions consisting of both PCTFE homopolymer as well as PCTFE copolymer. Generally, the PCTFE copolymers are PCTFE copolymers which may consist of up to about 50% by weight of at least one additional copolymerizable comonomer, including but not limited to: vinylidene fluoride, tetrafluoroethylene, and/or ethylene. It is to be clearly understood that plural copolymerizable comonomers may be used. The present invention further provides articles made from such PCTFE polymer resins which articles feature improved vapor barrier characteristics, improved machine processability, and which feature reduced encapsulated ash content in their composition.

In a further aspect, the present invention includes a process for the production of fluoropolymer compositions, such as a PCTFE homopolymer composition consisting essentially of a homopolymer having a desired molecular weight and which further exhibits a low residual ash content when compared to the redox processes of the prior art. The process of this invention utilizes the redox initiator system outlined above and further provides for the variance of the process conditions so to provide an effective process for a PCTFE polymer resin having a desired molecular weight within the range of 10,000 to 5,000,000.

Further disclosed are processes for the production of articles and structures which include at least one layer of the fluoropolymer resin, such as PCTFE polymer resin, which articles and structures feature resultant improvements in vapor barrier characteristics. Such PCTFE resin compositions as taught herein provide improved vapor barrier characteristics and improved machine processability and impart such characteristics to articles and structures of which they form a part, and impart improved processability of said PCTFE polymer resin.

Also disclosed in the present specification are shelf stable dispersions which include fluoropolymers, such as PCTFE homopolymers and/or PCTFE copolymers which exhibit a low tendency to coagulate, and which are easily redispersed, thus allowing for the dispersion to be maintained indefinitely. These suspensions are suitable for various coating applications and film formation on various substrates.

In accordance with present invention, there is provided a oxidation-reduction, i.e., "redox", process for the polymerization of fluoromonomers such as chlorotrifluoroethylene ("CTFE") which may be generally described as having a chemical formula of $CF_2$ = CFCl. CTFE is readily commercially available or may be produced by conventional process techniques.

In accordance with the present invention, the oxidation-reduction system includes the use of tert-butyl hydroperoxide, and sodium metabisulfite as reaction initiators.

Tert-butyl hydroperoxide (interchangeably referred herein to as "TBH"), may be represented as having the structure $(CH_3)_3COOH$.

Sodium metabisulfite (interchangeably referred to herein as "MBS") may be characterized as having the structure $Na_2S_2O_5$.

Both the TBH and the MBS may be provided in varying amounts for use in the polymerization of the fluoro-homopolymers.

While it is to be understood that other process conditions may be used and the benefits of the present invention still realized, in accordance with a preferred embodiment of the present invention, a quantity of fluoromonomer, such as CTFE, generally in a liquid form at room temperature, i.e., 20°C, is charged into a heatable reactor vessel which contains degassed, deionized water. The reactor is a closed vessel capable of withstanding internal pressure of at least 200 psi, preferably at least 1000 psi and is provided with a mechanical agitator which effectuates thorough mixing of the reactor contents. The heatable reactor vessel is also provided with a heat source which is capable of raising and lowering the temperature of the reactor vessel contents to the required reaction temperature while the reactants contained within the reactor vessel are agitated. The reactor vessel contents are raised to a temperature within the range from about 0°C to about 75°C or less. Also added continuously and/or in portions to the reactor vessel is a dilute aqueous solution of TBH and a dilute aqueous solution of MBS.

The presence of iron ions is needed to be present in the reactor. When iron is added, it may be in the form of ferrous sulfate, for example. In this case, it may be conveniently added together with the MBS stream.

The reaction is allowed to proceed until the liquid monomer is consumed, or in the alternative when there is noted a pressure drop in the reactor vessel which usually indicates the consumption of the liquid CTFE monomer within the reaction vessel. In accordance with the process of this invention, it has been found that the control of the reaction temperature is an important factor for establishing the final molecular weight of the PCTFE homopolymers being formed. It has been observed that generally the reaction temperature should not be allowed to get out of the range of between about 0°C to about 75°C, and preferably should stay between 5°C and about 60°C.

In alternative embodiments of processes according to the instant invention, the liquid CTFE polymer may be charged continuously to the reactor during the course of the reaction so to maintain a constant pressure, or alternately may be charged in a batchwise manner, in one or more batches, at any time during the course of the reaction. It is also contemplated that other water soluble hydroperoxides may be used in the stead of or in addition to the TBH described above. Further, the form of the reactor is not critical to the practice of process taught herein.

The process generally comprises the following steps: (a) charging the constituents to the reactor vessel, either in an initial batch or in a continuous manner during the course of the reaction, or in a semi-continuous manner, (b) initiation of the polymerization reaction and maintaining a controlled temperature throughout the reaction process, (c) allowing the reaction to proceed until the desired polymerization product is achieved, adjustment of the

agitation rate during the polymerization to prevent premature coagulation of the particles.

In accordance with step (a) of the process outlined above, any quantity of the CTFE monomer and optionally any additional comonomer is charged to a suitable reactor vessel. The constituents may be charged initially, or in a continuous manner during the course of the reaction, or in a semi-continuous manner. By "semi-continuous" is meant that a plurality of batches of the fluoromonomer, such as CTFE monomer and optionally any additional comonomers are charged to the reactor during the course of the polymerization reaction. A suitable reactor vessel includes but is not limited to conventional kettle type reactors, flasks, as well as any other sealable vessel which may be successfully used for the polymerization process. Of these the most preferred are conventional reactor kettles which are sealably closed and which may be pressurized to the required reaction pressures and preferably in excess of for safety considerations.

The constituents may be selected in quantities which are similar to those used for other redox or initiator type systems for the production of fluoropolymers, such as PCTFE polymers. By this it is to be understood that the specific redox system taught in the present specification may be used to substitute for other redox initiator type systems for other processes presently known in the art.

The proportion of the TBH and the MBS is critical to the success of the present invention but need be present in only an amount sufficient to successfully initiate the polymerization of the CTFE monomer and any additional copolymerizable comonomers within the

reactor vessel when the reactor contents are brought to their process conditions, and preferably the specific process conditions being outlined herein. Generally the concentration of the TBH in the solution used for initiation should be between about 0.01 grams to 10 grams per 100 ml of water at 20°C; preferably the TBH is present between about 0.1 grams and 5 grams per 100 cc of water at 20°C. The MBS is preferably present in an amount between about 0.01 grams to about 15 grams per 100 cc of water at 20°C; preferably the MBS is present between about 0.1 grams and 5 grams per 100 cc of water at 20°C.

In subsequent process step (b) the sealed reactor and its contents are heated or cooled to the reaction temperature, or alternately to a varying temperature profile which varies the temperature during the course of the reaction. The range of reaction temperatures is preferably between about 0°C up to and including about 75°C, although temperatures above and below these values are also contemplated.

The present inventors have found that the control of the temperature, the mode of addition, and the concentration of the initiator are important to the ultimate molecular weight of the final PCTFE polymer product produced as well as to the stability of the latex. The present inventors have found that at relatively higher reaction temperatures, a lower molecular weight product is produced, which effect is believed to be the result of more chain transfer in the reactor vessel. At relatively higher initiator concentrations, a lower molecular weight product is produced, which effect believed to be the result of more chain termination during particle growth. In light of these results, the inventors have found that

control of the reaction conditions to maintain a relatively higher reaction temperature and a relatively high initiator concentration provides the lowest molecular weight PCTFE polymer resin, while maintenance of a relatively low temperature and a relatively low concentration of the initiator, provides the highest molecular weight PCTFE polymer resin. Thereby, the inventors have found that variation of the reaction temperature is an important factor in the control of PCTFE molecular weight, and that control of the reaction temperature to a specified temperature is influential in determining the ultimate molecular weight of the resultant PCTFE polymer resin or dispersion being produced utilizing the types of redox system being taught herein. It will be apparent to the skilled practitioner that for a PCTFE aqueous dispersion having a desired molecular weight, that appropriate reaction conditions, viz., initiator concentration and reaction temperature, may be readily determined by conventional experimental techniques without undue experimentation, particularly in light of the Examples presented below.

Further, the present inventors have found that variation of the reaction temperature during the polymerization of the PCTFE homopolymer or PCTFE copolymer may result in PCTFE aqueous dispersions which have specific concentrations of PCTFE polymer chain lengths within particular ranges of molecular weight. By way of example, initially establishing the temperature of the reactor contents as a higher temperature, such as 50°C, and subsequently reducing the temperature and pressure of the reactor to a relatively lower pressure and temperature, such as 20°C

during the course of the reaction will provide a PCTFE polymer aqueous dispersion which leads to a PCTFE aqueous dispersion or resin of plural molecular weight range distributions; higher reactor pressure and temperature at the initiation of the reaction will provide a PCTFE dispersion having a relatively higher molecular weight, and subsequent operation of the reactor temperature and pressure during the course of the reaction provides a PCTFE dispersion having a relatively lower molecular weight. In a similar manner, the reaction conditions described immediately above may be reversed; e.g, lower initial temperature and pressure, followed by elevation of the temperature and pressure as the comonomers are consumed. Control of the temperature and pressure during the course of the polymerization reaction thereby provides a process for the production of PCTFE aqueous dispersions which have particular molecular weight ranges.

In accordance with this process step, temperature control is exerted upon the reactor vessel and its contents and such a desired temperature is set and maintained throughout the polymerization reaction. Any effective apparatus which provides the necessary cooling means to the reaction vessel and to the reactor contents may find use in conjunction with the inventive process being taught herein. Any conventional temperature control means may be used, such as those which include a temperature controller cooperatively operating with a heat source or heat sink, to provide or withdrawn heat from the reactor. One preferred example is a conventional temperature controlled bath within which the reactor is at least partially immersed. During the heating or cooling process, it is highly desirable that the rate of

agitation be controlled throughout the reaction so to provide optimal stirring of the reactor vessel contents to insure good mixing of the reactor contents, yet not cause coagulation of the polymer particles.

During the process step (b) the reactor pressure is modified only by the change in the internal pressure occasioned by the polymerization process itself. Desirably, a pressure sensing means be present in the reactor vessel so to provide an indication of the pressure of the vapor annulus within the reactor vessel, as the present inventors have found that a reduction in the vapor pressure within the vessel subsequent to the initiation of polymerization is the indicator that a substantial portion of the CTFE monomer has been polymerized. As indicated by a significant drop in pressure to that below the vapor pressure of liquid CTFE, whether it has been determined either by monitoring the pressure drop, by calculation of the reaction time, or any other time desired, the reaction vessel is vented and subsequently unsealed.

The present inventors have surprisingly found that the polymerized CTFE in the reaction vessel is a stable aqueous dispersion of PCTFE particles, generally in the size range of between about 0.01 - 1 micron. In addition, the particle size is very uniform in each batch (such as between about 0.2 to 0.25 micron). The polymer may be removed from the reactor and subsequently the water is driven off by any conventional means including evaporating, freeze-drying the aqueous suspension, or any other means, such as by the optional addition of a minor amount of an agglomerating or coagulating agent followed by

filtration or centrifuging. or the stable dispersion may be directly used in a coating application. The present inventors have further found the PCTFE polymer dispersion is highly stable and exhibits good shelf stability, generally in excess of several weeks when a dispersion is left undisturbed upon standing. Further, the present inventors have observed that after a PCTFE aqueous dispersion is left standing, it will eventually separate into a lighter aqueous phase, and a heavier precipitate phase which however may be readily reconstituted into a stable dispersion by mixing these two phases whereupon, the PCTFE dispersion reforms, and has been found to once again be highly stable and will remain stable once again for several weeks when a dispersion is left undisturbed upon standing. The PCTFE dispersion may be allowed to separate, and then reconstituted into the PCTFE dispersion by agitation indefinitely.

The present inventors have also surprisingly found that the dispersed PCTFE polymer particles formed according to the process taught herein are readily agglomerable from the dispersion formed within the reactor by the addition of a small amount of a coagulating agent. Such coagulating agents are typically acids, or monovalent or polyvalent salts. As is known to the art, the addition of such coagulating agents, especially in large amounts is frequently undesirable as they introduce ash into the polymer resin, and frequently require extensive washing for their removal in a subsequent step. This may be further complicated by the fact that the PCTFE particles formed by prior art production methods may be hydrophobic in their behavior.

The dispersed PCTFE particles are agglomerated by the introduction of relatively minor amounts of a coagulating agent and the reactor contents stirred to effect the agglomeration. Suitable coagulating agents include any coagulating agent or composition which are known to the art as effective in agglomerating other resin compositions, such as by the use of monovalent or polyvalent metal salts but are preferably dilute aqueous solutions of aluminum sulfate, $Al_2(SO_4)_3 \cdot 18 H_2O$, magnesium sulfate, $MgSO_4$, calcium chloride, $CaCl_2 \cdot 2 H_20$ as well as $AlCl_3 \cdot 6 H_20$, sodium or potassium carbonate or bicarbonate, sodium citrate, and the like. The concentration of these materials used to form the aqueous solutions are generally in the range of 1 % by weight and less based on the polymer. An advantageous feature of the use of such coagulant compositions in conjunction with the PCTFE dispersions taught herein is that such dispersions and their resulting PCTFE polymer resin compositions generally have essentially zero free ash (as on the order of 0 to 30 ppm). The rest of the cations present depend on the molecular weight of the polymer; the lower the molecular weight the higher is the content of sulfonic acid ends groups. The cations that are bound to the polymer depend on the degree of neutralization of polymer end groups. Such PCTFE polymer resin compositions are believed to be particularly useful in the production of formed and molded articles which are capable of being utilized in applications wherein contact with a foodstuff, medicament or imbibable composition is to be anticipated.

The PCTFE polymer resin may then be dried to provide a white free flowing particle composition consisting essentially of PCTFE polymer resin and any residual ash from the polymerization process. The intrinsic viscosity of the PCTFE polymer resin may be determined by conventional techniques, for example, by determining the intrinsic viscosity of a sample of the resin in a solvent such as 2,5-dichlorobenzotrifluoride wherein the intrinsic viscosity of the sample may be correlated to the numerical average molecular weight by the relationship:

$$[\ \eta\ ] = 6.15 \times 10^{-5}\ (M_\eta)^{0.74}$$

wherein "$(M_\eta)$" represents the number-average molecular weight. The intrinsic viscosity is determined at temperature sufficient to maintain the polymer is solution. For PCTFE resins, 2,5-dichlorobenzotrifluoride at 135°C provides a useful reference. This method well-known and described in, for example, Encyclopedia at 476.

A further testing method of determining the molecular weight of the PCTFE polymer resin compositions may be in accordance with the specifications outlined in ASTM-D 1430-81 from which a "Zero Strength Time", or "zst" is determined. Briefly, ASTM-D 1430-81 utilizes a compression molded test sample formed of the PCTFE polymer resin having dimensions of about 1.6 mm by 4.8 mm by 5.0 mm and which has a dual "v" shaped notch in the central portion of the test sample. The sample is suspended from one end with a 7.5 gram weight suspended frcm the

other end in an oven at 250°C. The zst value is the time in seconds after which the sample breaks.

Whereas the present specification has described in substantial detail the formation of the PCTFE polymer resin by use of the described redox system, it is to be clearly understood that the incorporation of comonomers including but not limited to vinylidene fluoride, tetrafluoroethylene and/or ethylene, may be utilized to form copolymers and terpolymers comprising the PCTFE described throughout this specification. Of these materials, the formation of PCTFE-vinylidene fluoride copolymers, and PCTFE-tetrafluoroethylene copolymers, and PCTFE-vinylidene fluoride, tetrafluoroethylene terpolymers are particularly contemplated.

Although this invention describes in detail a process leading to a stable, surfactant-free aqueous dispersion of fine particles of from about 0.1 to about 0.5 μm in diameter of CTFE and copolymers thereof, it is clearly understood that this technology is applicable to other fluoropolymers such as poly(tetrafluoroethylene) ("PTFE") and poly(vinylidene fluoride) ($PVF^2$"), as well as copolymers such as copolymers of tetrafluoroethylene ("TFE") with ethylene, propylene, perfluoropropene, perfluorovinyl ethers, vinylidene fluoride ($VF_2$"), mixtures thereof, and the like. Illustrative of suitable fluorocopolymers include, but are not limited to, fluorinated ethylene propylene ("FEP"), copolymers of TFE with perfluoroalkylperfluorovinyl ether ("PFA"), ethylene tetrafluoroethylene ("ETFE"), and ethylene chlorotrifluoroethylene ("ECTFE").

The compositions formed from the reaction taught herein following the process steps outlined may be used ultimately to form a variety of materials and articles in accordance with conventional processing techniques. By way of example, not by limitation, conventional processing techniques include any thermoforming technique wherein the PCTFE polymer resin is melted and/or plasticated and formed into an article or alternatively where the PCTFE polymer resin is applied to an article by technique which does not melt or plasticate it during its application. Examples of the former include conventional extrusion techniques, for the formation of fibers, strands, pellets, as well as formed profile shapes, and the like, as well as the formation of films, sheets, plates, by extrusion techniques through a flat film type die or by blown film methods, casting techniques wherein a billet of the PCTFE polymer resin is formed and an ultimate article is cut or profiled or otherwise derived from the billet, such as skiving film therefrom, as well injection and compression molding techniques wherein the plasticated PCTFE polymer resin composition is formed into a die or a mold of the latter. It is further contemplated that the shelf stable PCTFE polymer resin suspension taught herein may be incorporated into a variety of compositions which may be ultimately used in the formation or treatment of articles. Examples of such compositions include coatings including those useful in conjunction with films, molded articles and parts, extruded profiles, fabrics, fibers, as well as formed or molded articles including those which include polymer materials, metals, ceramics, as well as others

not particularly recited here. The coating compositions may be physically applied onto a surface such as by spraying, coating, dipping, and the like.

The invention is more easily understood by reference to specific embodiments which are representative examples according to the teachings of the instant invention. It must be understood, however, that the specific embodiments discussed herein are provided only for the purpose of illustration, and not by way of limitation, and it is to be further understood that the invention may be practiced otherwise than specifically described and yet be within the inventive scope.

**EXAMPLES**

In accordance with the teaching of the present specification a plurality of PCTFE aqueous dispersions and resins, both PCTFE homopolymer resins and PCTFE copolymer resins were produced. For the production of PCTFE copolymer resins, amounts of vinylidine fluoride were used as the comonomer.

Various process conditions including variation of the temperatures, starting monomers as well as different batch sizes were utilized in the production of the PCTFE aqueous dispersions and are indicative of the broad range of process conditions within which the present invention may be practiced; exemplary process conditions are outlined in the Examples below.

**Polymerization Process Conditions - 4 Liter Reactor**

A pressurizable stainless steel reactor having an internal volume of four liters equipped with a mechanical stirrer, and conventional inlet and outlet ports was used. The mechanical stirrer comprised a rotatable shaft fitted with two sets of four blades

each, wherein each set of blades may be generally described as flat paddle blades set at an angle of approximately 45° relative to the shaft. The two sets of blades were located upon the shaft with a proximal spaced-apart distance of approximately six inches, and further, direction of the angle of each of one set of blades was in a direction opposite to that of the other set of blades; such a configuration desirably ensured the most effective mixing of the reactor contents. The other end of the shaft was affixed to an electric motor which is used to rotate the shaft. The reactor was further provided with a temperature control system which included a heating bath which operated in conjunction with a temperature controller to assure the maintenance of a desired temperature within the reactor.

In the production of a PCTFE aqueous dispersion, in a first process step approximately 1700 ml of degassed deionized water at a temperature in the range 5°C to 55°C was charged to the sealed reactor through an inlet port and subsequently the gas space within the reactor was purged with nitrogen so to remove any residual atmospheric oxygen. Thereafter, in the case of the production of a PCTFE homopolymer, approximately 320 ml of liquid CTFE was metered into the reactor through an appropriate liquid inlet port; in the case where the production of a PCTFE copolymer was to be produced, approximately 320 ml of liquid CTFE and the appropriate mass proportion of the comonomer, such as $VF_2$ (vinylidine fluoride), was also provided at this time. The temperature control system was activated to assure that the reactor and its contents were brought to a desired reaction

temperature, and the mechanical stirrer was activated so to maintain an optional level of mixing throughout the polymerization process. Previously prepared degassed separate aqueous solutions of TBH and MBS were then metered into the reactor at a predetermined rate to initiate the polymerization of the monomer constituents. Optionally, in certain cases, the use of a small amount of iron in the form of $FeSO_4 \cdot 7\ H_2O$ was also introduced into the reactor.

The polymerization of the monomer constituents was allowed to proceed until the total designated time had lapsed, or until a drop in the pressure of the gas within the reactor was noted at which time the addition of the initiator was stopped and then stirring continued for an additional time period of about 30 minutes.

Upon the completion of polymerization, the reactor vessel was vented, flushed with gaseous $N_2$, and opened to yield a stable aqueous dispersion of polymer particulates. This aqueous dispersion can then be used as the primary constituent in a fluoropolymer coating or it can be coagulated into resin. These particulates were finely divided and generally had a mean particle diameter of about 0.1 to about 0.2 microns. In order to facilitate the separation of the particles in the subsequent centrifuging operation, a coagulating agent known as useful with PCTFE polymers was used. The specific coagulating agents were one of the following:

| Type: | Coagulating Agent: |
|---|---|
| A | $AlCl_3 \cdot 6\ H_2O$ |
| B | $Al_2(SO_4) \cdot 18\ H_2O$ |
| C | $CaCl_2 \cdot 2\ H_2O$ |
| D | $MgSO_4$ |
| NaCl | sodium chloride |
| HCl | hydrochloric acid |

These coagulating agents were added in the form of an aqueous solution in amounts, generally about 1-5 grams dissolved in 200 ml of water to the reactor contents and stirred until the particles were agglomerated. Generally, the time required varied between minutes to about 3 hours.

The contents of the reactor were then provided to a conventional bench top centrifuge with a five inch stainless steel perforated basket which was operated to separate the liquid portion of the reactor contents from the solid polymer particulates which were collected in a fitted polyethylene terephthalate bag. A batchwise manner of operation was used as the available centrifuge did not have the capacity to simultaneously separate and wash all of the polymer particles in one batch. The collected particulates were subsequently washed on the centrifuge with two to four liters of purified deionized water, and then dried upon a glass tray in a circulating air oven at a temperature of 100°C for a period of 14-18 hours.

The polymer particles recovered were caked, but could be ground into a dry, fluffy free-flowing powder.

**Polymerization Process Conditions - 10 Gallon Reactor**

A stainless steel pressurizable reactor having an internal volume of 10 gallons and equipped with a mechanical stirrer, and with conventional inlet and outlet ports was used. The mechanical stirrer comprised a rotatable shaft fitted with two sets of four blades each having a configuration generally the same as was described for the process utilizing the four liter reactor, and a jacketed temperature control system as well.

The production of PCTFE resins was generally in accordance with the procedure outlined in conjunction with the description of the polymerization process used with the four liter reactor; approximately 24-25 liters of purified degassed water were used, and a further distinction was that the stirrer was operated to rotate at 350 rpm in the 10 gallon reactor.

Upon the completion of polymerization, the reactor vessel was flushed with $N_2$, vented and opened to yield a suspension of polymer particles. A two liter aliquot was subsequently coagulated as described above, then centrifuged and washed in a batchwise manner in a conventional centrifuge as outlined above; a batchwise manner was used as the centrifuge did not have the capacity to simultaneously separate and wash all of the polymer particles. The polymer particle yield was dried as outlined above, and yielded a dry cake which could be easily ground into a free-flowing powder.

**Evaluation of the Polymer Reaction Product**

The dried polymer particles were quantitatively evaluated and characterized.

The intrinsic viscosity of the polymer was determined in accordance with the conventional technique utilizing a solution of the polymer in 2,5-dichlorobenzotrifluoride at 135 °C.

The number-average and weight-average molecular weight was determined utilizing a Waters Model 150-C Gas Pressure Chromatograph using a Zorbax trimodal column having 3000Å, 300Å and 60Å diameter pores in conjunction with a viscosity detector which utilized a 0.1 % solution of the particular polymer being tested in 2,5- dichlorobenzotrifluoride at a temperature of 145°C and a flow rate of 1 ml/minute. The "heterogeneity index" of the polymer is determined to be the ratio of weight average molecular weight (Mw) divided by the number average molecular weight (Mn).

The melt viscosity of the particular polymer sample being evaluated was performed using a Rheometric Dynamic Spectrometer using 25mm diameter disks in parallel plate mode. First, a test disc having a thickness of approximately 3-4 millimeters was allowed to equilibrate at 240°C for 5 minutes. Subsequently the polymer sample was evaluated in conjunction with conventional evaluative procedures; a frequency sweep from 500 to 0.1 radians/sec with a 2% strain.

The viscosity was reported at 0.1 radians/second, and the total time for the test was 10 minutes.

**Example Compositions**

Examples 1-3: As is particularly described on Table 1, reaction conditions, the specific quantities of the comonomers, here both CTFE and varying amounts of the comonomer $VF_2$ were provided to the four liter reactor and processed in accordance with the procedure

described under the heading "Polymerization Process Conditions - 4 Liter Reactor" above, and evaluated in accordance with the general guidelines outlined above under the heading "Evaluation of the Polymer Reaction Product". The polymers produced in accordance with the various process conditions were evaluated, and the results of such evaluation is outlined on Table 2, following.

Example 4: The reaction was carried out as per Examples 1-3, but the reactor contents further included the addition of 3.5 grams of $CHCI_3$ which was included to evaluate its use as a chain transfer agent. Evaluation results are outlined on Table 2.

Example 5: The comonomers CTFE and $VF_2$ were provided to the four liter reactor and processed in accordance with the procedure described under the heading "Polymerization Process Conditions - 4 Liter Reactor" above, and evaluated in accordance with the general guidelines outlined above under the heading "Evaluation of the Polymer Reaction Product". The polymer produced in the reactor was divided into two portions, and evaluated and reported as samples labeled "5a" and "5b". The results of the evaluation are outlined on Table 2.

Example 6: The comonomers CTFE and $VF_2$ were provided to the four liter reactor and processed in accordance with the procedure described under the heading "Polymerization Process Conditions - 4 Liter Reactor" above and within the process constraints outlined on Table 1, with the additional distinction that 1530 ml of purified deionized water and 170 ml of glacial acetic acid were included in the reactor in the place of the 1700 ml of purified deionized water.

The polymer produced was evaluated as per Examples 1-3, and the results are outlined on Table 2.

Examples 7-8: The comonomers CTFE and $VF_2$ and a minor amount of an iron compound, ferrous sulfate ($FeSO_4$ $7H_20$) were provided to the four liter reactor and processed in accordance with the procedure described under the heading "Polymerization Process Conditions - 4 Liter Reactor" above and within the process constraints outlined on Table 1. The resultant polymer was recovered, dried and evaluated with the results as outlined on Table 2.

Examples 9-14: Compositions comprising CTFE monomers with and without the comonomer $VF_2$ were produced according to the guidelines given above in the four-liter reactor; the resultant polymer product was evaluated and the evaluation results are outlined on Table 2.

Examples 15-17: The polymer compositions according to these examples were produced utilizing the procedures described above under the heading "Polymerization Process Conditions - 10 Gallon Reactor" as outlined above and utilizing the specific constituents and conditions particularly described in Table 3, below.

The resultant polymers are recovered and evaluated in accordance with the procedures outlined described under the heading "Evaluation of the Polymer Reaction Product" and the results of such evaluations are outlined on Table 4, below.

Example 18: Twenty liters of deionized water was added to a clean, glass lined ten gallon reactor. The system was sparged with a nitrogen stream for one hour to remove oxygen. To the closed reactor was added 3.4 kg. of chlorotrifluoroethylene and 120 g. vinylidene

fluoride. The reactor contents were warmed to 45°C and while stirring efficiently, the polymerization was initiated by concurrently pumping solution of 6.75g of 70% aqueous t-butylhydroperoxide in 100 ml of purified water and 5.7 g sodium metabisulfite plus 1.8 g. $FeSO_4 \cdot 7H_2O$ in 200 ml purified water over a 15 minute period. During the course of the polymerization solutions of 36g 70% aqueous t-butylhydroperoxide in 500 ml of purified water and 27.9 g sodium metabisulfite plus 0.75g. $FeSO_4$ $7H_20$ in 500 ml of purified water were pumped into the reactor concurrently at the rate of 50 ml/hr. The initial reactor pressure was about 180 psi. There was a slight exotherm due to the polymerization reaction causing a temperature rise to 46°C and a pressure increase to 185 psi. The polymerization temperature was controlled to 45°C± 1° C by circulating tempered water through the reactor jacket. At 1.1 hours and 3.5 hours, after observing a 10 psi drop in reactor pressure, additional monomers, 3.45 kg chlorotrifluoroethylene plus 110 g vinylidene fluoride and 2.2 kg. chlorotrifluoroethylene plus 70 g vinylidene fluoride respectively, were added to the reactor. After 5.2 hours, the reactor pressure had dropped to 70 psi and the pumping of the sodium metabisulfite solution into the reactor was terminated. The t-butylhydroperoxide solution was continued for 0.5 hours to ensure complete reaction of any sodium bisulfite in the reaction mixture. The reactor was vented and swept with a nitrogen stream to remove any unreacted chlorotrifluoroethylene. The polymer was in suspension as submicron particles. The

reaction mixture plus two gallons of rinse water had a polymer content of about 25 % by weight.

The polymer was recovered from a 500 ml aliquot by coagulating, while stirring, by the addition of 1 ml of conc. $H_2SO_4$. The coagulated polymer was stirred for 1 hour and the polymer was recovered by centrifuging. The centrifuge cake was washed with one liter of purified water plus two ml conc. $H_2SO_4$, one liter of purified water, two liters of purified water plus four grams of sodium bicarbonate, and then six liters of purified water. The polymer was dried overnight at 95°C in a circulating air oven. A white powdery polymer was recovered (110g) which had an intrinsic viscosity of 0.67 and a melt viscosity of $1.2 \times 10^5$ Pa-seconds.

It will be appreciated that the instant specification and examples set forth herein are by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention, whose limitations are bounded only by the appendant claims.

What is Claimed:

1. A process for forming fluoropolymers or a copolymer of a fluoromonomer and at least one copolymerizable monomer which comprises:

(a) forming a polymerization reaction mixture comprising a monomer selected from the group consisting of a fluoromonomer and a combination of a fluoromonomer and at least one copolymerizable monomer, and a redox initiator system comprising a mixture of an alkyl hydroperoxide and an alkali metal metabisulfite in a reaction solvent comprising water; and

(b) polymerizing said monomer while maintaining said mixture at a controlled temperature in said mixture to form a stable, soap free, aqueous dispersion of said fluoropolymer or said copolymer.

2. The process according to claim 1 wherein said redox initiator system comprises tert-butyl hydroperoxide and sodium metabisulfite.

3. The process according to claim 1 which comprises:

(a) charging said monomer to a reactor vessel;

(b) charging to said reactor vessel said redox initiator system and maintaining a controlled temperature throughout the reaction process; and

(c) allowing the reaction to proceed to form said fluoropolymer or said copolymer.

4. The process according to claim 1 wherein said fluoropolymer is a homopolymer selected from the group consisting of tetrafluoroethylene, vinylidene fluoride, and chlorotrifluoroethylene, and said copolymer is a copolymer of tetrafluoroethylene and at least one comonomer selected from the group consisting

of vinylidene fluoride, perfluorovinyl ethers, propylene, perfluoropropene, and mixtures and copolymers thereof.

5. The process according to claim 1 wherein said fluoropolymer is a homopolymer selected from the group consisting of tetrafluoroethylene, vinylidene fluoride, and chlorotrifluoroethylene, and said copolymer is selected from the group consisting of ethylene with fluorinated propylene, ethylene with perfluoroalkylperfluorovinyl ether, and ethylene with chlorotrifluoroethylene and mixtures thereof.

6. The process according to claim 1 including further coagulating of said aqueous dispersion, filtering of the resultant coagulant and washing of said coagulant, to thereby form a precipitate of said fluoropolymer or said copolymer.

7. The process according to claim 6 including further drying of said precipitate.

8. A stable, aqueous, soap-free dispersion of a fluoropolymer or a copolymer of a fluoromonomer and a copolymerizable monomer produced by the process of claim 1.

9. A fluoropolymer or a copolymer of a fluoromonomer and a copolymerizable monomer produced by the process of claims 1, 6 or 7.

10. An article formed from the fluoropolymer or copolymer of claim 8.

11. An article comprising at least one layer formed from the fluoropolymer or copolymer of claim 8.

# INTERNATIONAL SEARCH REPORT

Intern: I Application No
PCT/uS 96/00643

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F14/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| P,X | US,A,5 453 477 (B.C. OXENRIDER ET AL.) 26 September 1995<br>see the whole document | 1-11 |
| A | EP,A,0 106 956 (ALLIED CORP.) 2 May 1984 | 1 |
| A | DATABASE "CHEMICAL ABSTRACTS" (HOST: STN):<br>abs. 118: 81 612, Colombus, OH, USA;<br>& SU-A-1 712 363 (A.A. KUZNETSOV et al.):<br>"Polymerization catalysts for manufacturing poly(alpha, beta, beta-trifluorostyrene) 15 February 1992 | 1 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"&" document member of the same patent family

1

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 12 April 1996 | 29.04.96 |
| **Name and mailing address of the ISA**<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. ( + 31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: ( + 31-70) 340-3016 | **Authorized officer**<br>Glikman, J-F |

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...ormation on patent family members

Interna Application No
PCT/US 96/00643

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| | | JP-C- | 1699992 | 14-10-92 |
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